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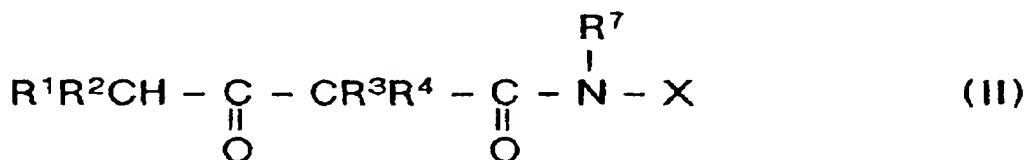
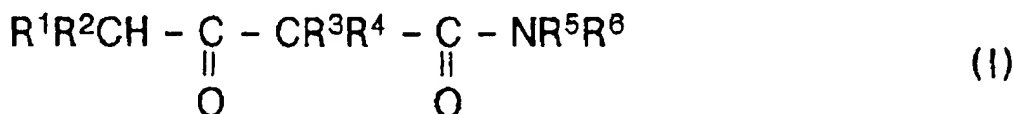
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- (72) KOKEL, Nicolas, DE
(72) GYOPAR RAU, Maria, DE
(72) FISCHER, Gerhard, DE
(72) GULBINS, Erich, DE
(71) BASF AKTIENGESELLSCHAFT, DE
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(30) 1996/11/21 (196 47 982.7) DE
(54) **DISPERSIONS RENFERMANT DES POLYURETHANES AVEC
DES GROUPES CARBONYLES DANS LA FRACTION
CETONIQUE**
(54) **DISPERSIONS CONTAINING POLYURETHANES HAVING
CARBONYL GROUPS IN KETO FUNCTION**



(57) Dispersions aqueuses renfermant un polyuréthane (A), contenant des unités structurales dérivées de composés de formule (I) (voir formule I), dont les substituants ont les significations suivantes : R¹, R², R³ représentent indépendamment de l'hydrogène, un alkyle C₁-C₂₄ ou un alcényle C₆-C₂₄; R⁴ représente de l'hydrogène; R⁵, R⁶ (a) représentent ensemble un alcanediyle C₄-C₁₀, (b) représentent chacun un alkyle C₂-C₁₀, un cycloalkyle C₅-C₈ ou un aralkyle C₇-C₂₀, (c) représentent chacun un poly(oxyde d'alkylène C₂-C₄) terminé par un hydroxyle, ou (d) l'un des radicaux R⁵ ou R⁶ a la signification spécifiée en (a), (b) ou (c), et l'autre est un hydrogène ou un radical de formule II (voir formule II), dans lequel X représente un alcanediyle C₂-C₆, R⁷ ayant la même signification que R⁵ ou R⁶, excepté que R⁷ ne représente pas un radical de formule II, où les radicaux R⁵ et R⁶ dans chacun des cas (a) et (d) portent en tout un (1) groupe hydroxyle lié à un atome de carbone aliphatique, facultativement R⁵ et (ou) R⁶ peut

(57) Aqueous dispersions containing a polyurethane(A) having structural units derived from compounds of the formula (I) (see formula I) in which the substituents have the following meanings: R¹, R², R³ independently denote hydrogen, C₁-C₂₄ alkyl or C₆-C₂₄ alkenyl R⁴ denotes hydrogen R⁵, R⁶ (a) together denote C₄-C₁₀ alkanediyl, (b) each denotes C₂-C₁₀ alkyl, C₅-C₈ cycloalkyl or C₇-C₂₀ aralkyl, (c) each denotes a hydroxyl-terminated poly(C₂-C₄ alkylene oxide), or (d) one radical R⁵ or R⁶ has the meaning stated under (a) to (c) and the other is hydrogen or a radical of the formula II (see formula II) in which X denotes C₂-C₆ alkanediyl and R⁷ has the same meaning as R⁵ or R⁶ except that R⁷ does not denote a radical of the formula II, where the radicals R⁵ and R⁶ in each of the cases (a) and (d) carry a total of one (1) hydroxyl group attached to an aliphatic carbon atom, optionally the radical R⁵ and/or R⁶ carries 1 or 2 hydroxyl groups bonded to an aromatic carbon atom or one nitrile, tertiary amino, carboxylic acid or sulfonic acid group which are optionally present in the





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ou peuvent porter 1 ou 2 groupes hydroxyles liés à un atome de carbone aromatique ou à un groupe nitrile, amino tertiaire, acide carboxylique ou acide sulfonique, qui sont facultativement présents sous la forme de leurs sels; la valence fonctionnelle moyenne (F) de tous les constituants structurels du polyuréthane (A) est de 1,5 à 2,2, valeurs fondées sur les valences fonctionnelles intervenant au cours de la synthèse du polyuréthane (A) dans une réaction d'addition.

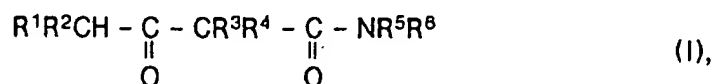
form of their salts, and the average functionality (F) of all structural components of the polyurethane (A) is from 1.5 to 2.2, based on the functionalities which interreact during the synthesis of the polyurethane (A) in an addition reaction.



Dispersions Containing Polyurethanes Having Carbonyl Groups In Keto Function

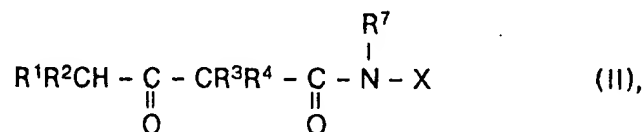
Description

The present invention relates to aqueous dispersions containing a polyurethane(A) having structural units derived from compounds of the formula (I)



in which the substituents have the following meanings:

- $\text{R}^1, \text{R}^2, \text{R}^3$ independently denote hydrogen, $\text{C}_1\text{-C}_{24}$ alkyl or $\text{C}_6\text{-C}_{24}$ alkenyl
- R^4 denotes hydrogen
- R^5, R^6
- a) together denote $\text{C}_4\text{-C}_{10}$ alkanediyl,
 - b) each denotes $\text{C}_2\text{-C}_{10}$ alkyl, $\text{C}_5\text{-C}_8$ cycloalkyl or $\text{C}_7\text{-C}_{20}$ aralkyl,
 - c) each denotes a hydroxyl-terminated poly($\text{C}_2\text{-C}_4$ alkylene oxide), or
 - d) one radical R^5 or R^6 has the meaning stated under (a) to (c) and the other is hydrogen or a radical of the formula II



in which

X denotes $\text{C}_2\text{-C}_8$ alkanediyl and

R^7 has the same meaning as R^5 or R^6 except that R^7 does not denote a radical of the formula II,

where

- the radicals R^5 and R^6 in each of the cases (a) and (d) carry a total of one (1) hydroxyl group attached to an aliphatic carbon atom,
- optionally the radical R^5 and/or R^6 carries 1 or 2 hydroxyl groups bonded to an aromatic carbon atom or one nitrile, tertiary amino, carboxylic acid or sulfonic acid group which are optionally present in the form of their salts, and
- the average functionality (F) of all structural components of the polyurethane (A) is from 1.5 to 2.2, based on the functionalities which interreact during the synthesis of the polyurethane (A) in an addition reaction.

Aqueous dispersions containing polyurethanes are well known (*cf* D. G. Oertel "Kunststoff Handbuch 7", 2nd Edition 1983, Carl Hanser Verlag Munich Vienna, *pp* 24 to 25 and *pp* 571 to 574). It is also known that it is possible to use the polyurethane dispersions as coating compositions, *eg* as coating compositions or printing inks.

From a processing and economical point of view and with regard to the desirable properties of the coatings produced from the coating compositions the polyurethane dispersions must in this case comply with a number of requirements not hitherto satisfied to the required extent.

Coating compositions are frequently required to satisfy the following conditions with reference to their performance characteristics:

- The coating compositions should be storable for a lengthy period of time without the properties thereof (*eg* rheological properties) or the properties of the coatings produced therefrom changing and without generating gas, since the formation of gas makes storage in tightly sealed containers virtually impossible.
- The coating compositions should contain minimal amounts of solvents, levelling agents or other readily volatile organic components, in order to minimize the emissions of organic compounds when applying and drying the coating compositions.
- Following application to the workpiece the coating composition should dry or cure rapidly so that it is ready for use or can be further processed after only a short period of time.
- During processing of the coating compositions they should show a minimum tendency to foam.

High-quality coatings and surfaces of polyurethane coating compositions are required to satisfy a combination of the following conditions:

- Smooth surface and high gloss
- Resistance to moisture, steam and chemicals such as dilute alkalis and acids and also organic solvents or surfactants
- Insensitivity to mechanical stresses such as impact, shock or friction
- No intrinsic color or defects such as bubbles or cracks
- In the case of wood as substrate the coating compositions should cause the visible structure of the wood to become more evident (inflammation).

The development of coatings having such a combination of properties is hampered by the fact that the individual processing properties appear to be based on diverging structural properties. Whilst the abrasion resistance demands a certain degree of hardness, the impact strength requires a certain degree of elasticity. Furthermore a glossy surface requires good levelling characteristics of the coating composition, which generally demands use of volatile organic compounds as levelling agents.

In particular the coating compositions should be capable of being processed by a maximum number of conventional processes. The various processes involving various expenditure, where the expenditure correlates with the quality the produced therewith, are required, to make it possible to prepare coatings as economically as possible which satisfy a very specific quality level; for an increase in expenditure is often justified only when there is a corresponding increase in the quality level. On the other hand the user is confronted by considerable logistic problems if he is to have at hand a different coating composition starting material for each processing method. A particularly important part is played by the following processing methods:

The cold-curing process (final curing of the coating at room temperature) using a single-component coating system is the least elaborate and should satisfy moderate quality requirements.

The cold-curing process using a two-component coating system, which complicates the process for the user on account of the fact that he has to blend the

coating system and the restricted processing time he has to complete blending, should satisfy more stringent quality requirements.

The baking method (final curing at temperatures usually of from 100° to 160°C) is suitable for the preparation of coatings meeting the highest quality standards.

Printing inks should usually satisfy the same criteria as regards their performance characteristics, as have already been mentioned with regard to the coating compositions (varnishes). On the other hand, the fulfilment of further demands that are specific to printing inks is important:

- High concentration of solid materials and particularly pigments so that the drying times are minimal and
- good levelling characteristics on polar and non-polar substrates such as polyethylene and polypropylene

Requirements to be met by articles printed with the printing inks, particularly those comprising non-polar plastics materials, are:

- Good adhesion of the inks to the substrate especially under the action of water
- Resistance of the inks to conventional solvents, fats, surfactants, aqueous solutions, acids and alkalis
- Good fastness properties.

Even in the case of this set of criteria conflicts of aims result in some instances, which are only insufficiently solved using the printing inks of the prior art. It is known, for example, that the levelling characteristics of the printing inks can be improved by the addition of surfactant; however, the applied inks exhibit a lack of resistance to water. The wettability can also be improved by the addition of solvent, which, however restricts the ecological advantages of the water-based inks.

Polyurethane dispersions which are suitable for use as single-component systems for coating various substrates are described in EP-B 0,332,326. They contain not only a water-dispersible polyurethane having a molecular weight of more than 2000 and carrying carbonyl groups in keto or aldehyde function, but also a further component carrying hydrazine or hydrazone groups or the polyurethane carries

hydrazine or hydrazone groups in addition to the carbonyl groups in keto or aldehyde function. In order to insert the structural element of the carbonyl groups into the polyurethane, it is recommended to use, in the preparation thereof, monomers such as dihydroxy acetone, the Michael adduct of diacetone acrylamide with diamine or alkanolamine or the Michael adduct of 2 mol of diacetone acrylamide with 2 mol of diamine.

A disadvantage of the dispersions that are prepared using dihydroxy acetone is however that the films that are prepared therewith are colored brown.

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Another proposal made in this reference is to incorporate keto groups into the polyurethane by using monomers such as the Michael adduct of diacetone acrylamide with diethanolamine. These can be processed by the cold-curing process in a single-component system to form coatings having satisfactory properties but are not suitable for use as one-component or two-component systems for the preparation of coatings having superior properties. Neither does processing by the baking method yield coatings of high quality.

Furthermore, aqueous dispersions containing a water-dispersible polyurethane containing carbonyl groups and a polyhydrazide are revealed in DE-A 3,837,519. According to this teaching, the carbonyl function is incorporated in the polyurethane by using, during preparation thereof, mono- or poly-alcohols containing carbonyl groups, *eg* monohydroxy alkyl ketones such as hydroxyacetone, hydroxybenzaldehyde, acetoin, benzoin, adducts of diepoxides with ketocarboxylic acid and also ketocarboxylate containing at least one hydroxyl group. Another recommendation made in this paper is to use these dispersions as varnishes or printing inks.

These monomers cannot be used automatically, since problems relating to, say, low reactivity, intrinsic color of the polymer or stability of the dispersion occur.

The two aforementioned classes of compounds suffer from another drawback, *ie* they are only useful for a very restricted number of cross-linking possibilities.

Furthermore, esters of pyruvic, acetoacetic or levulinic acid with polyols are included under the keto monomers containing one or more alcoholic hydroxyl groups described in DE 3,837,519. An important drawback resulting from the use of these ester derivatives is their tendency to become hydrolyzed in the dispersion prepared therefrom. During storage, the free acid is gradually eliminated, as a result of which the cross-linking efficiency declines. During the hydrolytic degradation of dispersions containing acetoacetic ester alcohol, gas formation

takes place. Storage of these dispersions in sealed containers is consequently associated with a considerable potential hazard. The levulinate exhibits, in addition, reduced reactivity, since the ketocarbonyl group possesses no activating group in the immediate vicinity. The use of the pyruvate produces colored polymers.

DE-A 4,406,547 describes cross-linkable polyurethanes that are functionalized with olefinic double bonds and CH-acidic groups and are present dispersed in water. For the preparation thereof, a hydroxyl-terminated, substantially linear and solvent-free polyurethane is caused to react with a low molecular weight ester. Esterification produces polyurethanes containing terminal β -functional ester groupings.

This process is not generally useful, since for example "harder" or branched-chain polyurethanes exhibiting a high viscosity cannot be modified without the use of a solvent for viscosity reduction. Low-boiling solvents which would be capable of being removed from the dispersion by distillation, cannot be used, since the temperature that is required for the transesterification stage cannot be achieved. If the solvent boils at a higher temperature, it is then no longer possible for it to be removed from the dispersion.

Even when use is made of temperatures which are so high that a direct result is thermal damage to the polyurethane, the total reaction of all hydroxyl groups of the polyurethane cannot be guaranteed, as is also evident from the article "Novel synthesis of low VOC polymeric dispersion and their application in waterborne coatings" in the 21st Int. Conf. Organ. Coat. Sci. Technol. Athens, pp 55-68 (1995), particularly page 60, by B. Vogt-Birnbrich.

The dispersions produced by this process likewise have a high tendency to become hydrolyzed and develop gas during storage.

Coatings comprising dispersions containing a polyurethane which is composed of the said hydroxycarbonyl compounds can still not give complete satisfaction as regards their mechanical properties and resistance to solvents. In addition, these dispersions show a tendency toward coagulation.

The non-prepublished German patent application bearing the file number 19618675.7 describes aqueous dispersions containing a polyurethane which is likewise composed of alcohols having carbonyl groups in keto function. These alcohols proposed therein differ from those used in the present invention in the number of alcohol groups present. Said reference concerns polyfunctional

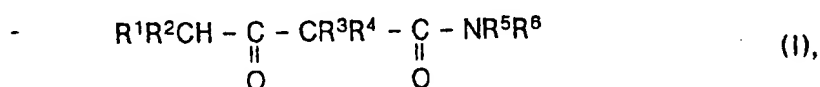
alcohols.

It is thus an object of the present invention to provide aqueous coating compositions having a high overall level of application properties, which do not exhibit the deficiencies of the prior art, and in the processing of which to form glossy heavy-duty coatings no or only relatively small amounts of volatile levelling auxiliaries need to be used. In particular, the coating compositions should be usable in as wide a range as possible, that is to say, the property level of the coatings that is attainable therewith should not fall short of that of the prior art when using various processing methods.

Another object of the invention is to provide printing inks which do not exhibit the deficiencies of the prior art and which make it possible to produce, in particular, printed non-polar substrates to which the ink adheres permanently.

Accordingly, we have found the dispersions described above.

The dispersions contain a polyurethane (A), which is composed of compounds of the formula (I)



in which the substituents generally have the following meanings:

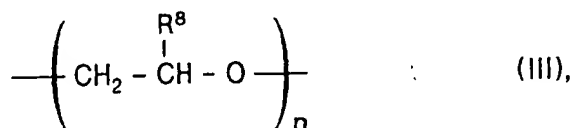
$\text{R}^1, \text{R}^2, \text{R}^3$ independently denote hydrogen, $\text{C}_1\text{-C}_{24}$ alkyl or $\text{C}_6\text{-C}_{24}$ alkenyl

R^4 denotes hydrogen,

R^5, R^6 a) together form $\text{C}_4\text{-C}_{10}$ alkanediyl, preferably butane-1,4-diyl and pentane-1,5-diyl,

b) each denotes $\text{C}_2\text{-C}_{10}$ alkyl, more preferably C_2 and C_3 alkyl or $\text{C}_5\text{-C}_8$ cycloalkyl, preferably cyclopentyl or cyclohexyl or $\text{C}_7\text{-C}_{20}$ aralkyl, preferably benzyl,

c) each denotes a hydroxyl-terminated poly($\text{C}_2\text{-C}_4$ alkylene oxide), preferably a radical of the formula III



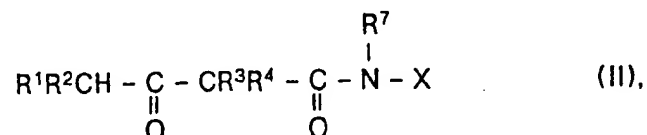
in which

R^8 denotes hydrogen, methyl and/or ethyl and

n is an integer from 1 to 10

or

d) one of the radicals R^5 and R^6 has the meaning stated under (a) to (c) and the other radical is hydrogen or a radical of the formula II



in which

X denotes C_2-C_8 alkanediyl and

R^7 has the same meaning as R^5 or R^6 with the exception of the radical of formula II.

where

- the radicals R^5 and R^6 together carry one hydroxyl group attached to an aliphatic carbon atom and, optionally,
- the radical R^5 and/or R^6 carries one or two hydroxyl groups bonded to an aromatic carbon atom or one nitrile, tertiary amino, carboxylic acid or sulfonic acid group optionally present in the form of their salts
- the average functionality (F) of all structural components, based on the functionalities which occur during synthesis of the polyurethane, being from 1.5 to 2.2, preferably from 1.7 to 2.0, and more preferably from 1.8 to 1.95.

The person skilled in the polyurethane art is well aware of the fact that the molecular weight can be controlled by the choice of the average functionality of the starting materials which interreact in an addition reaction to form urethane or urea groups, *ie* those containing isocyanate, alcohol, primary amine and secondary

amine groups. Since the compounds of the formula (I) are monofunctional with respect to the synthesis of the polymer chain of the polyurethane, it will generally be necessary to use not only the difunctional starting materials usually employed but also trifunctional compounds and compounds of higher functionality.

The average functionality (F) is defined by the quotients

$$F = \frac{\text{number of moles of all isocyanate groups and isocyanate-reactive groups}}{\text{number of moles of all structural components}}$$

The functional groups taken into consideration for the calculation of F are not only isocyanate groups and alcohol groups attached to aliphatic carbon atoms but also other groups which react with isocyanates in an addition reaction and which react at a similar rate or even more rapidly than said alcohols, that is to say, for example, primary amine and secondary amine groups. On account of their greater inertness, hydroxycarbonyl groups and hydroxyl groups bonded to an aromatic carbon atom are not taken into account however.

With regard to the desired density of cross linkage and the mechanical properties dependent thereon, the concentration of the carbonyl groups of the structural elements in the polyurethane which are derived from the compounds of the formula (I) is made to be such that generally from 3 to 140, preferably from 6 to 100, more preferably from 10 to 90 mmol of these groups are present per 100 g of polyurethane.

The preparation of the aqueous dispersions of the invention usually takes place by

I. Preparation of a polyurethane by causing the reaction of

a) polyvalent isocyanates containing from 4 to 30 carbon atoms,

b) polyols, of which

b1) from 10 to 100 mol, based on the total weight of the polyols (b), have a molecular weight of from 500 to 5000 and

b2) from 0 to 90 mol, based on the total amount of the polyols (b), are difunctional and have a molecular weight of from 62 to 500 g/mol,

c) compounds of the formula I,

d) optionally other polyvalent compounds containing reactive groups and differing from the monomers (b) and (c), said groups being alcoholic hydroxyl groups or primary or secondary amino groups and

e) monomers differing from monomers (a), (b), (c) and (d) and containing at least one isocyanate group or at least one isocyanate-reactive group and which additionally carry at least one hydrophilic group or a potentially hydrophilic group, by which means the polyurethanes are rendered water-dispersible.

II. Dispersion of the polyurethane obtained in step I in water.

Suitable monomers (a) are the polyisocyanates usually employed in polyurethane chemistry.

Examples of particularly suitable monomers are diisocyanates $X(NCO)_2$, where X stands for an aliphatic hydrocarbon radical containing from 4 to 12 carbon atoms, a cycloaliphatic or aromatic hydrocarbon radical containing from 6 to 15 carbon atoms or an araliphatic hydrocarbon radical containing from 7 to 15 carbon atoms.

Examples of such diisocyanates are tetramethylene diisocyanate, hexamethylene diisocyanate, dodecamethylene diisocyanate, 1,4-diisocyanatocyclohexane, 1-isocyanato-3,5,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI), 2,2-bis-(4-isocyanatocyclohexyl)propane, trimethylhexane diisocyanate, 1,4-diisocyanatobenzene, 2,4-diisocyanatotoluene, 2,6-diisocyanatotoluene, 4,4'-diisocyanatodiphenylmethane, tetramethylxylylene diisocyanate (TMXDI), 2,4'-diisocyanatodiphenylmethane, p-xylylene diisocyanate, the isomers of bis(4-isocyanatocyclohexyl)methane such as the trans/trans, the cis/cis and the cis/trans isomers and also mixtures of these compounds.

Important mixtures of these isocyanates are particularly the mixtures of the respective structural isomers of diisocyanatotoluene and diisocyanatodiphenylmethane; particularly suitable is a mixture of 80 mol of 2,4'-diisocyanatotoluene and 20 mol of 2,6-diisocyanatotoluene. Furthermore mixtures of aromatic isocyanates such as 2,4'-diisocyanatotoluene and/or 2,6-diisocyanatotoluene with aliphatic or cycloaliphatic isocyanates such as hexamethylene diisocyanate or IPDI are particularly advantageous, the preferred component ratio of the aliphatic to aromatic isocyanates being from 4:1 to 1:4.

The compounds (a) used may also be isocyanates which carry not only free isocyanate groups but also other hidden isocyanate groups, eg uretdione or

carbodiimide groups.

Optionally, isocyanates may be included which carry only one isocyanate group. The concentration thereof is generally not more than 10 mol%, based on the total molar content of the monomers. The monoisocyanates usually carry other functional groups such as olefinic groups or carbonyl groups and serve to introduce functional groups into the polyurethane which enable dispersion or cross linkage or other polymer-like reactions of the polyurethane to take place. Suitable monomers for this purpose are monomers such as isopropenyl- α,α -dimethylbenzyl isocyanate (TMI).

To increase the average functionality (F), use may be made of, eg, trivalent and tetravalent isocyanates. Such isocyanates are obtained, for example, by effecting interreaction of divalent isocyanates by converting a portion of their isocyanate groups to allophanate, biuret or isocyanurate groups. Commercially available compounds are for example the isocyanurate or biuret of hexamethylene diisocyanate.

Other suitable polyisocyanates of higher functionality are eg polyisocyanates exhibiting urethane groups and based on 2,4- and/or 2,6-diisocyanatotoluene, isophorone diisocyanate or tetramethylene diisocyanate on the one hand and low molecular weight polyhydroxy compounds such as trimethylol propane on the other hand.

Suitable polyols as regards good film formation and elasticity are (b) mainly polyols of higher molecular weight, preferably diols (b1) having molecular weights of from approximately 500 to 5000, preferably from approximately 1000 to 3000 g/mole.

The polyols (b1) concerned are, in particular, polyester polyols described in, eg, Ullmanns Encyklopaedie der technischen Chemie, 4th Edition, Vol. 19, pp 62 to 65. Preferably use is made of polyester polyols obtained by the reaction of divalent alcohols with divalent carboxylic acids. Instead of the free poly(carboxylic acid)s, the corresponding poly(carboxylic anhydride)s or corresponding polycarboxylates of lower alcohols or mixtures thereof may be used for the preparation of the polyester polyols. The poly(carboxylic acid)s can be aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic and be optionally substituted by, eg, halogen atoms and/or be unsaturated. Examples of suitable compounds are: suberic acid, azelaic acid, phthalic acid, isophthalic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylene tetrahydrophthalic anhydride, glutaric anhydride, maleic acid, maleic anhydride, fumaric acid, and dimeric fatty acids. Preferred are dicarboxylic acids of

amines, *eg* water, ethylene glycol, propane-1,2-diol, propane-1,3-diol, 1,2-bis(4-hydroxydiphenyl)propane or aniline. Particularly preferred is polytetrahydrofuran having a molecular weight of from 240 to 5000, and preferably from 500 to 4500.

Also suitable are polyhydroxy olefins, preferably those containing 2 terminal hydroxyl groups, *eg* α,ω -dihydroxypolybutadiene, α,ω -dihydroxypolymethacrylate or α,ω -dihydroxypolyacrylate, as monomers (b1). Such compounds are disclosed, for example, in EP-A 0,622,378. Other suitable polyols are polyacetals, polysiloxanes and alkyd resins.

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The polyols can also be used as mixtures in any desired proportions.

The hardness and the modulus of elasticity of the polyurethanes can be raised when the polyols (b) used are not only the polyols (b1) but also diols (b2) of even lower molecular weight, *ie* having a molecular weight of from approximately 62 to 500, preferably from 62 to 200 g/mole.

The monomers (b2) used are primarily the structural components of the short-chain alkane diols specified for the preparation of polyester polyols, where neopentyl glycol and the unbranched diols having from 2 to 12 carbon atoms and an even number of carbon atoms are preferred.

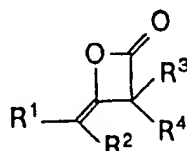
The concentration of of the polyols (b1), based on the total amount of polyols (b) is preferably from 10 to 100 mol% and the concentration of the monomers (b2), based on the total amount of the polyols (b) is preferably from 0 to 90 mol%. Particularly preferred is a ratio of the polyols (b1) to the monomers (b2) of from 0.2:1 to 5:1, and more preferably from 0.5:1 to 4:1.

Suitable components (c) are primarily compounds of the formula (I).

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The compounds of formula (I) can be obtained by causing a diketene of the formula (IV)

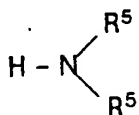
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(IV)

to react with an alkanolamine of the formula (V)

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(V)

the general formula $\text{HOOC}-(\text{CH}_2)_Y-\text{COOH}$, in which Y is an integer from 1 to 20, preferably an even number from 2 to 20, eg succinic acid, adipic acid, dodecanoic acid and sebacic acid.

- 5 Suitable polyvalent alcohols are eg ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,3-diol, butene-1,4-diol, butyne-1,4-diol, pentane-1,5-diol, neopentyl glycol, bis(hydroxymethyl)cyclohexanes such as 1,4-bis(hydroxymethyl)-cyclohexane, 2-methylpropane-1,3-diol, methylpentane diols, also diethylene glycol, triethylene glycol, tetraethylene glycol, poly(ethylene glycol), dipropylene glycol, poly(propylene glycol), dibutylene glycol and poly(butylene glycol)s.
10 Preferred are neopentyl glycol and alcohols of the general formula $\text{HO}-(\text{CH}_2)_x$, in which x is an integer from 1 to 20, preferably an even number from 2 to 20. Examples of these are ethylene glycol, butane-1,4-diol, hexane-1,6-diol, octane-1,8-diol and dodecane-1,12-diol.

15

Furthermore, polycarbonate diols are also suitable, such as can be prepared by, say, the reaction of phosgene with an excess of the low molecular weight alcohols specified as structural components for the polyester polyols.

- 20 Also suitable are polyester diols based on lactones, these being homopolymers or mixed polymers of lactones, preferably addition products of lactones with suitable difunctional starting molecules, said addition products having terminal hydroxyl groups. Suitable lactones are preferably those derived from compounds of the general formula $\text{HO}-(\text{CH}_2)_z$, in which z is an integer from 1 to 20. Examples are ϵ -caprolactone, β -propiolactone, γ -butyrolactone and/or methyl- ϵ -caprolactone
25 and mixtures thereof. Suitable starting components are eg the dihydric alcohols of low molecular weight specified above as structural components for the polyester polyols. The corresponding polymers of ϵ -caprolactone are particularly preferred. It is also possible to use lower polyester diols or polyether diols as starters for the
30 preparation of the lactone polymers. Instead of the polymers of lactones use may be made of the corresponding chemically equivalent polycondensates of hydroxycarboxylic acids corresponding to the lactones.

The polyesterols can also be composed of minor amounts of mono- and/or poly-
35 functional monomers.

Other suitable monomers (b1) are polyether diols. They can be obtained, in particular, by polymerization of ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorohydrin with itself, eg in the presence of
40 BF_3 , or by the addition of these compounds, optionally in admixture or successively, to starting components containing reactive hydrogen atoms, such as alcohols or

the general formula $\text{HOOC}-(\text{CH}_2)_Y-\text{COOH}$, in which Y is an integer from 1 to 20, preferably an even number from 2 to 20, eg succinic acid, adipic acid, dodecanoic acid and sebacic acid.

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40 BF_3 , or by the addition of these compounds, optionally in admixture or successively, to starting components containing reactive hydrogen atoms, such as alcohols or

amines, *eg* water, ethylene glycol, propane-1,2-diol, propane-1,3-diol, 1,2-bis(4-hydroxydiphenyl)propane or aniline. Particularly preferred is polytetrahydrofuran having a molecular weight of from 240 to 5000, and preferably from 500 to 4500.

Also suitable are polyhydroxy olefins, preferably those containing 2 terminal hydroxyl groups, *eg* α,ω -dihydroxypolybutadiene, α,ω -dihydroxypolymethacrylate or α,ω -dihydroxypolyacrylate, as monomers (b1). Such compounds are disclosed, for example, in EP-A 0,622,378. Other suitable polyols are polyacetals, polysiloxanes and alkyd resins.

10

The polyols can also be used as mixtures in any desired proportions.

The hardness and the modulus of elasticity of the polyurethanes can be raised when the polyols (b) used are not only the polyols (b1) but also diols (b2) of even lower molecular weight, *ie* having a molecular weight of from approximately 62 to 500, preferably from 62 to 200 g/mole.

The monomers (b2) used are primarily the structural components of the short-chain alkane diols specified for the preparation of polyester polyols, where neopentyl glycol and the unbranched diols having from 2 to 12 carbon atoms and an even number of carbon atoms are preferred.

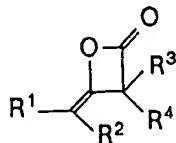
The concentration of of the polyols (b1), based on the total amount of polyols (b) is preferably from 10 to 100 mol% and the concentration of the monomers (b2), based on the total amount of the polyols (b) is preferably from 0 to 90 mol%. Particularly preferred is a ratio of the polyols (b1) to the monomers (b2) of from 0.2:1 to 5:1, and more preferably from 0.5:1 to 4:1.

Suitable components (c) are primarily compounds of the formula (I).

30

The compounds of formula (I) can be obtained by causing a diketene of the formula (IV)

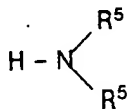
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(IV)

to react with an alkanolamine of the formula (V)

40



(V)

in an addition reaction.

In the diketenes of formula (IV) or the amines of formula (V) the radicals R¹, R², R³ and R⁴ or the radicals R⁵, R⁶ and R⁷, respectively, have the same meanings as specified for the compound of formula (I).

It is particularly preferred to use a diketene in which the radicals R¹, R² and R³ denote hydrogen or one of the radicals R¹ or R² denotes hydrogen and the other radical R¹ or R² and the radical R³ denote a linear, saturated, unsubstituted
 10 hexadecyl radical.

Particularly preferred alkanolamines are ethanolamine, *N*-methylethanolamine, *N*-ethylethanolamine, *N*-butylethanolamine, *N*-cyclohexylethanolamine, *N*-*tert*-butylethanolamine, leucinol, isoleucinol, valinol, prolinol, hydroxyethylaniline, 2-(hydroxymethyl)piperidine, 3-(hydroxymethyl)piperidine, 2-(2-hydroxyethyl)piperidine, 2-amino-2-phenylethanol, 2-amino-1-phenylethanol, ephedrine, *p*-hydroxyephedrine, norephedrine, adrenaline, noradrenaline, serine, isoserine, phenylserine, 1,2-diphenyl-2-aminoethanol, 3-amino-1-propanol, 2-amino-1-propanol, 2-amino-2-methyl-1-propanol, isopropanolamine, *N*-ethylisopropanolamine, 2-amino-3-phenylpropanol, 4-amino-1-butanol, 2-amino-1-butanol, 2-aminoisobutanol, neopentanolamine, 2-amino-1-pentanol, 5-amino-1-pentanol, 2-ethyl-2-butyl-5-amino-pentanol, 6-amino-1-hexanol, 2-amino-1-hexanol, 2-(2-aminoethoxy)ethanol, 3-(aminomethyl)-3,5,5-trimethylcyclohexanol, 2-aminobenzylalcohol, 3-aminobenzylalcohol, 2-amino-5-methylbenzylalcohol, 2-amino-3-methylbenzylalcohol, 3-amino-2-methylbenzylalcohol, 3-amino-4-methylbenzylalcohol, 3-amino-6-methylbenzylalcohol, 1-aminoethyl-4-hydroxybenzylalcohol, 2-(4-aminophenyl)ethanol, 2-(2-aminophenyl)ethanol, 1-(3-aminophenyl)ethanol, serine, homoserine, threonine, ethanolaminoacetic acid, 4-amino-3-hydroxybutyric acid, *N*-(2-hydroxyethyl)-glycinnitrile, 4-(2-hydroxyethyl)piperazine and 1-amino-4-(2-hydroxyethyl)-piperazine, 2-hydrazinoethanol or diaminomonools, such as *N*-(2-aminoethyl)-ethanolamine, 1-[2-(2-hydroxyethoxy)ethyl]piperazine, 1,3-diamino-2-propanol
 25 may also be used.

Preferred adducts of formula I are those containing the diketene in which the
 35 radicals R¹, R² and R³ each denote hydrogen. Particularly preferred is
 $\text{CH}_3\text{C}(=\text{O})-\text{CH}_2-\text{C}(=\text{O})-\text{NH}-\text{CH}_2-\text{CH}_2-\text{OH}$.

The preparation of the compounds of formula (I) can be carried out, for example, in the manner described for the acetoacetamide derivatives in the patent
 40 specifications DE 1,142,859 and GB 715,896.

The monomers (d) which differ from the components (b) and diols (c) generally serve to increase the average functionality (F). They are generally more than dihydric non-aromatic alcohols, amines containing two or more primary and/or secondary amino groups and also compounds which carry in addition to one or more alcoholic hydroxyl groups one or more primary and/or secondary amino groups.

Alcohols which are more than dihydric are *eg* trimethylol propane, pentaerythritol glycerol or sugar and their ethoxylation products.

10 Polyamines containing 2 or more primary and/or secondary amino groups are primarily used when the chain growth or cross linkage should take place in the presence of water, since amines usually react more quickly than alcohols or water with isocyanates. This is frequently necessary when aqueous dispersions of
15 branched-chain polyurethanes or polyurethanes of high molecular weight are desired. In such cases the procedure adopted is to prepare prepolymers containing isocyanate groups and then to rapidly disperse the same in water and subsequently increase the chain length or effect cross linkage by the addition of compounds containing a plurality of amino groups reactive with isocyanate.

20 Suitable amines for this purpose are generally polyfunctional amines in the molecular weight range of from 32 to 500 g/mole, preferably from 60 to 300 g/mole, which contain at least two primary, two secondary or one primary and one secondary amino group. Examples thereof are diamines such as diamino-
25 ethane, diaminopropanes, diaminobutanes, diaminohexanes, piperazine, 2,5-dimethylpiperazine, amino-3-aminomethyl-3,5,5-trimethylcyclohexane (isophoronediamine, IPDA), 4,4-diaminodicyclohexylmethane, 1,4-diaminocyclohexane, aminoethylethanolamine, hydrazine, hydrazine hydrate or triamines such as diethylene triamine, triethylene tetramine or 1,8-diamino-4-aminomethyloctane.

30 The amines can also be used in blocked form, *eg* in the form of the corresponding ketimines (*cf eg* CA 1,129,128), ketazines (*cf eg* the US-A 4,269,748) or amine salts (*cf* US-A 4,292,226). Oxazolidines such as are used, for example, in US-A 4,192,937 are also hidden polyamines which can be used for the preparation of
35 the polyurethanes of the invention to effect chain growth of the prepolymers. When using such hidden polyamines they are generally mixed with the prepolymers in the absence of water and this mixture is subsequently mixed with the dispersant water or a portion of the dispersant water so that the corresponding polyamines are liberated hydrolytically.

The polyurethanes preferably contain no polyamine or from 1 to 10, more preferably from 1.5 to 5 mol%, based on the total amount of the components (b), (c) and (d), of a polyamine having at least 2 amino groups which are reactive with isocyanates, as monomers (d).

5 Furthermore, minor amounts of monoalcohols can be used to effect chain stoppage, *ie* preferably in amounts of less as 10 mol%, based on components (b) and (d). The function thereof is generally similar to that of the monoisocyanate, *ie* they mainly serve to effect functionalization of the polyurethane having free-
10 radically polymerizable C=C double bonds.

In order to make the polyurethanes water-dispersible, the polyurethanes are not only composed of the components (a), (b), (c) and (d) but also of monomers (e) differing from the components (a), (b), (c) and (d) and carrying at least one
15 isocyanate group or at least one isocyanate-reactive group and in addition at least one hydrophilic group or a group capable of being converted to hydrophilic groups. Below, the term "hydrophilic groups or potentially hydrophilic groups" is abbreviated to "(potentially) hydrophilic groups". The (potentially) hydrophilic groups react with isocyanates much more slowly than the functional groups of the
20 monomers which are used for the synthesis of the main polymer chain.

The concentration of the components containing (potentially) hydrophilic groups based on the total amount of the components (a), (b), (c), (d) and (e) is generally such that the molar magnitude of the (potentially) hydrophilic groups, based on the
25 weight of all monomers (a) to (e), is from 30 to 1000, preferably from 50 to 500 and more preferably from 80 to 400 mmol/kg.

The (potentially) hydrophilic groups can be non-ionic or preferably (potentially) ionic hydrophilic groups.

30 Particularly suitable non-ionic hydrophilic groups are poly(ethylene glycol ether)s comprising preferably from 5 to 100, more preferably from 10 to 80, recurring ethylene oxide units. The concentration of polyethylene oxide units is generally from 0 to 10, preferably from 0 to 6 wt%, based on the weight of all monomers (a)
35 to (e).

Preferred monomers containing non-ionic hydrophilic groups are the reaction products of a poly(ethylene glycol) and a diisocyanate carrying a terminal etherified poly(ethylene glycol) radical. Such diisocyanates and processes for the
40 preparation thereof are described in the patent specifications US 3,905,929 and

US 3,920,598.

Ionic hydrophilic groups are primarily anionic groups such as the sulfonate, carboxylate and phosphate groups in the form of their alkali metal or ammonium salts and also cationic groups such as ammonium groups, particularly protonized tertiary amino groups or quaternary ammonium groups.

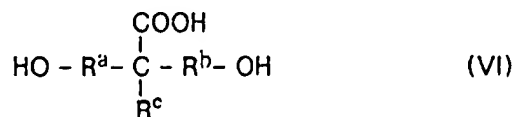
Potentially ionic hydrophilic groups are primarily those which can be converted by simple neutralisation, hydrolysis or quaternizing reactions to the aforementioned ionic hydrophilic groups, that is to say, for example, carboxylic acid groups, anhydride groups or tertiary amino groups.

(Potentially) ionic monomers (e) are described in detail in, *eg*, Ullmanns Encyklopaedie der technischen Chemie, 4th Edition, Vol. 19, *pp* 311-313 and for example in DE-A 1,495,745.

(Potentially) cationic monomers (e) are primarily monomers containing tertiary amino groups of special practical significance, for example: tris(hydroxyalkyl)-amines, *N,N*-bis(hydroxyalkyl)alkylamine, *N*-hydroxyalkyldialkylamine, Tris(aminoalkyl)amines, *N,N*-bis(aminoalkyl)alkylamines, *N*-aminoalkyldialkylamines, where the alkyl radicals and alkanediyl units in these tertiary amines independently contain from 2 to 6 carbon atoms. Also suitable are polyethers containing tertiary nitrogen atoms and preferably containing two terminal hydroxyl groups, such as can be prepared, *eg*, by alkoxylation of two amines having hydrogen atoms attached to amine nitrogen, *eg* methylamine, aniline, or *N,N*-dimethylhydrazine, in conventional manner. Such polyethers generally have a molecular weight between 500 and 6000 g/mole.

These tertiary amines are converted to the ammonium salts either with acids, preferably strong mineral acids such as phosphoric acid, sulfuric acid, hydrohalic acids or strong organic acids or by reaction with suitable quaternizing agents such as C₁ to C₆ alkyl halides, *eg* bromides or chlorides.

Suitable monomers containing (potentially) anionic groups are usually aliphatic, cycloaliphatic, araliphatic or aromatic carboxylic acids and sulfonic acids carrying at least one alcoholic hydroxyl group or at least one primary or secondary amino group. Preferred are dihydroxyalkylcarboxylic acids, primarily containing from 3 to 10 carbon atoms, such as are also described in US-A 3,412,054. We particularly prefer compounds of the general formula VI



5 in which R^a and R^b stand for a C_1 to C_4 alkanediyl unit and R^c stands for a C_1 to C_4 alkyl unit, especially dimethylolpropionic acid (DMPA).

Also suitable are corresponding dihydroxysulfonic acids and dihydroxyphosphonic acids such as 2,3-dihydroxypropanephosphonic acid.

10

Also suitable are dihydroxyl compounds having a molecular weight of more than 500 to 10000 g/mole and containing at least 2 carboxylate groups, which are disclosed in DE-A 3,911,827. They can be prepared by the reaction of dihydroxyl compounds with tetraoic dianhydrides such as pyromellitic dianhydride or
15 cyclopentanetetracarboxylic dianhydride in a molar ratio of from 2:1 to 1.05:1, in a polyaddition reaction. Particularly suitable dihydroxyl compounds are the monomers (b2) mentioned as chain extenders and also the polyols (b1).

Suitable monomers (e) containing isocyanate-reactive amino groups are amino-
20 carboxylic acids such as lysine, β -alanine, the adducts, mentioned in DE-A 2,034,479, of aliphatic diprimary diamines with α,β -unsaturated carboxylic acids such as *N*-(2-aminoethyl)-2-aminoethanecarboxylic acid and also the corresponding *N*-aminoalkylaminoalkylcarboxylic acids, where the alkanediyl units contain from 2 to 6 carbon atoms.

25

If monomers containing potentially ionic groups are used, they can be converted to the ionic form before or during, but preferably after, the isocyanate polyaddition reaction, since the ionic monomers in the reaction mixture frequently dissolve only with difficulty. We particularly prefer that the carboxylate groups be present in the
30 form of their salts with an alkali ion or an ammonium ion as counterion.

Effective amounts of compounds which are structurally related to those of the formula (I) and which differ from those of formula (I) only in that the radicals R carry not just 1 but from 2 to 5 hydroxyl groups attached to aliphatic carbon atoms,
35 are used for the preparation of the polyurethanes (A) of the invention not in effective amounts and are preferably not used at all. These compounds structurally related to those of formula (I) are described in the non-published German application bearing the file number 19618675.7.

40 Normally are the components (a), (b), (c), (d) and (e) and also the respective

molar amounts thereof are selected such that the ratio of A to B where

- A) is the molar concentration of isocyanate groups and
- 5 B) is the sum of the molar concentration of the hydroxyl groups and the molar concentration of the functional groups which can react with isocyanate in an addition reaction.

is from 0.5:1 to 2:1, preferably from 0.8:1 to 1.5:1, and more preferably from
10 0.9:1 to 1.2:1. Most preferably the ratio A:B is as near to 1:1 as possible.

Not only the components (a), (b), (c), (d) and (e) but also monomers containing only one reactive group are generally used in amounts of up to 15 mol%, preferably up to 8 mol%, based on the total amount the components (a), (b), (c), (d) and (e).

15 The polyaddition of the components (a) to (e) generally takes place at reaction temperatures of from 20 to 180 °C preferably from 50 to 150 °C under standard pressure or under autogenous pressure.

20 The necessary reaction times may range from a few minutes to some hours. It is known in the art of polyurethane chemistry that the reaction time is influenced by a number of parameters such as temperature, concentration of the monomers and reactivity of the monomers.

25 In order to accelerate the reaction of the diisocyanates, conventional catalysts, such as dibutyltin dilaurate, tin(II) octoate or diazabicyclo-(2,2,2)-octane, can be used.

Suitable polymerizing equipment comprises stirred boilers, particularly when
30 solvents are used to lower the viscosity and provisions are made for good heat dissipation.

If the reaction is to be carried out in substance, extruders are particularly suitable by reason of the high viscosities usually encountered and the usually very brief
35 reaction times, especially self-cleaning multiscrew extruders.

The dispersions are usually prepared by one of the following processes:

Using the "acetone process", an anionic polyurethane is prepared from the
40 components (a) to (e) in a water-miscible solvent boiling under standard pressure below 100 °C. Water is added until a dispersion forms in which water is the

coherent phase.

The "prepolymers mix process" differs from the acetone process in that there is first of all formed, instead of a completely reacted (potentially) anionic polyurethane, a prepolymer carrying isocyanate groups. The components (a) to (d) used are in this case dimensioned such that the defined ratio A:B is greater than 1.0 to 3 and is preferably from 1.05 to 1.5. The prepolymer is first of all dispersed in water and subsequently cross-linked by reaction of the isocyanate groups with amines carrying more than 2 isocyanate-reactive amino groups or chain-extended
10 with amines carrying 2 isocyanate-reactive amino groups. Chain growth takes place even when no amine is added. In this case isocyanate groups are hydrolyzed to amine groups which react with those isocyanate groups which still remain in the prepolymers to cause chain growth.

15 If a solvent has been used in the preparation of the polyurethane, the major portion of the solvent is removed from the dispersion, for example by distillation under reduced pressure. Preferably, the dispersions show a solvent concentration of less than 10 wt% and are more preferably free from solvents.

20 The dispersions generally have a solids concentration of from 10 to 75, preferably from 20 to 65 wt% and a viscosity of from 10 to 500 m-Pas (measured at a temperature of 20 °C and a shearing rate of 250 s⁻¹).

25 The aqueous dispersions of the invention are usually virtually free from polyvalent metal ions.

Hydrophobic auxiliaries which are possibly difficult to distribute homogeneously in the finished dispersion, such as phenol condensation resins of aldehydes and phenol or phenol derivatives or epoxy resins and other polymers specified, eg, in
30 DE-A 3,903,538, 4,309,079 and 4,024,567, and which are used in polyurethane dispersions for example as adhesion promoters, may be added to the polyurethane or the prepolymers before dispersion takes place by the methods that are described in the two specifications mentioned above. Suitable hydrophobic auxiliaries are specified, for example, in DE-A 3,903,538, 4,024,567 and
35 4,309,079.

In one variant of the present invention the polyurethane dispersions of the invention are modified with free-radically polymerizable monomers containing a C=C double bond and not exhibiting any isocyanate groups or isocyanate-reactive
40 groups (monomers f). In this case said monomers are primarily those usually employed in the preparation of emulsion polymers.

Suitable monomers (f) are, *eg*, the C₁ to C₆ alkyl esters of (meth)acrylic acid and also lauryl acrylate and butane diol diacrylate or compounds containing carbonyl groups, such as *eg* methylvinyl ketone, (meth)acrolein, crotonaldehyde, diacetone (meth)acrylamide, diacetone (meth)acrylate.

5 Other monomers are *eg* vinyl esters of carboxylic acids containing up to 20 carbon atoms such as vinyl laurate, vinyl stearate, vinyl acetate and vinyl propionate, vinyl aromatic compounds containing up to 20 carbon atoms such as styrene and vinyl toluene, ethylenically unsaturated nitriles such as acrylonitrile and methacrylo-
10 nitrile, ethylenically unsaturated amides such as acrylamide and methacrylamide, vinyl halides such as vinyl chloride and vinylidene chloride and aliphatic hydrocarbons containing from 2 to 8 carbon atoms and having 1 or 2 C=C double bonds, such as butadiene and ethylene.

15 The monomer (f) may be added during the synthesis of the polyurethane (A), prior to dispersion of the polyurethane (A), or it can be added to the aqueous dispersion containing the polyurethane (A), and subjected to free radical polymerization by conventional methods. For this purpose radical forming polymerization initiators are added to the mixture of the polyurethane dispersion and the monomer (f). Further-
20 more, the monomer (f) can be metered as a feed to a polyurethane dispersion containing initiator.

If it is desired to cause grafting of the polymer formed from the monomer (f) to the polyurethane, it is recommendable to additionally use, during synthesis of the
25 polyurethane, monomers containing a free-radically polymerizable C=C double bond.

In order to cause cross linkage of the polyurethane (A), there is usually added to the aqueous dispersion a cross-linking agent (b) which exhibits functional
30 substituents which react with the structural units derived from compounds of the formula (I), in an addition or condensation reaction. Such cross-linking agents (b) are for example compounds containing at least one aldehyde group or at least 2 functional substituents, selected from the group consisting of: primary amino group, secondary amino group, hydrazine group, hydrazide group, aminooxy group,
35 isocyanate group or blocked isocyanate group.

Suitable polyamines are *eg* non-polymeric amines, such as ethylenediamine, diethylenetriamine, triethylenetetramine, propylenediamine, butylenediamine, 1,6-hexanediamine, 1,12-dodecanediamine, cyclohexylenediamine, piperazine, 2-
40 methylpiperazine, isophoronediamine, phenylenediamine, tolylenediamine, xylylene-

diamine, 4,4-diaminodiphenylmethane, menthane-diamine and *m*-xylenediamine. The reactive amino compound can also be a polymer such as an acrylic resin, a polyester resin or a polyurethane resin containing amino groups, a poly(propylene oxide) containing amino groups (jeffamines), or a polyethyleneimine.

5 These amines can be used in blocked form if desired, that is to say in the form of their aldimines or ketimines. These blocked amines are well known and are described, for example, by K. J. Kim and R. C. Williams in "Proceedings of the annual Waterborne and Higher Solids Symposium, New Orleans, 57, (1993)" and
10 by B. Vogt-Birnbrich in "Proceedings of the 21st International Conference in Organic Coatings, Athens, 55, (1995)" and also in EP-A 552,469 and EP-A 584,818. Use is preferably made of amines blocked with aromatic aldehydes such as benzaldehyde.

15 Suitable polyhydrazides are *eg* dicarboxylic dihydrazides as described, for example, in EP-A 442,652, page 11, line 52 to page 12, line 1. These are preferably derived from dicarboxylic acids, of which the polyesterdiols which can be used as component (b1) are also composed. Furthermore use can also be made of the corresponding polyhydrazone derivatives, *eg* those derived from acetone or
20 butanone.

Other suitable polyhydrazides having improved water solubility are described, *eg*, in EP-A 629,657.

25 Furthermore, suitable cross-linking agents (b) are polyisocyanates having a cross-linking action caused by transimination. Such compounds are described, for example, in DE-A 4,121,946.

Cross-linking agents containing aminooxy groups, which may also be used in the
30 form of their salts, are disclosed, *eg*, in EP-A 516,074 or DE-A 4,219,384.

Another cross-linking method consists in the addition of aldehydes containing one or more aldehyde groups, which may be protected if desired, to the dispersion of the invention.

35 Suitable monoaldehydes are *eg* compounds of the formula $X-R^9-CHO$, in which R^9 denotes a C_1 to C_8 alkanediyl radical and X is a hydrogen atom or a hydroxycarbonyl radical. Preferred aldehydes are formaldehyde, acetaldehyde and benzaldehyde.

40 Suitable polyfunctional aldehydes are low molecular weight compounds, particular-

ly aliphatic aldehydes of the formula $\text{OCH}-(\text{CH}_2)_n-\text{CHO}$, in which n is an integer from 0 to 8, preferably from 0 to 4, such as glyoxal or glutaric dialdehyde.

It is also possible to use oligomers, polymers or copolymers of ethylenically unsaturated, free-radically polymerizable aldehydes as cross-linking component. Suitable ethylenically unsaturated, free-radically polymerizable aldehydes are *eg* acrolein, methacrolein, formylstyrene and hydroxymethylfurfuryl (meth)acrylate. Such cross-linking components can, if they are not sufficiently soluble, be dispersed in the aqueous phase of the dispersion and take part in film formation when the dispersion is used as binding agent. Oligomers or polymeric cross-linking components of this kind having a molecular weight of from 1000 to 500,000 (weight average) are preferred.

By protected aldehyde groups we mean corresponding derivatives having a comparable reactivity to that of the free aldehyde groups themselves. Acetals, mercaptals and mercaptols, dioxolanes and dithiolanes are for example suitable. Acetal or dioxolane groups which have been formed in the reaction of aldehyde groups with alkanols having from 1 to 4 carbon atoms in the alkyl radical or with alkanediols containing 2 or 3 carbon atoms in the alkylene are preferred.

Examples of unsaturated monomers having protected aldehyde functions are diethoxypropyl acrylate and diethoxypropyl methacrylate and (meth)acryloyloxypropyl-1,3-dioxolan.

Other suitable aldehyde derivatives are aldimine compounds which have been prepared by the reaction of an optionally substituted aromatic or heteroaromatic aldehyde with an optionally polyfunctional primary amine. These compounds are well known and are described, *eg*, in EP 552,469 A3 or in US-P 5,451,653.

Cross linkage can also take place via Michael acceptors. Suitable Michael acceptors are well known compounds described in DE-A 4,237,492.

Generally the cross linkage is carried out by Michael addition in the presence of a catalyst. Suitable catalysts are Lewis bases or Brønstedt bases, such as are described in DE-A 4,237,492.

The amounts of components (A) and (B) are preferably such that the molar ratio of the carbonyl groups of the structural elements derived from the compounds of the formula (I) to the functional substituents of the compounds (B) is from 0.1:1 to 10:1, preferably from 1.5:1 to 0.5:1.

Other suitable cross-linking agents (B) are aminoplastic resins, *eg* melamine/formaldehyde condensates such as are described by D.H. Solomon in *The Chemistry of Organic Filmpolymers*, *pp* 235 *et seq*, John Wiley & Sons, New York, 1967. These are preferably melamine/formaldehyde condensation resins having a molecular weight of from 20 to 1000 and more preferably they are the partially or completely etherified derivatives thereof. The degree of etherification is preferably at least 45 % based on the maximum possible etherification. The melamine/formaldehyde condensates are etherified with monoalcohols of from 1 to 4 carbon atoms, such as methanol, ethanol, propanol and preferably butanol, and/or monoethers of diols containing a total of from 2 to 7 carbon atoms.

The melamine/formaldehyde condensates can however be partially replaced, if desired, by other cross-linking aminoplastics, such as are described in *eg* "Methoden der organischen Chemie" (Houben-Weyl), Vol. 14/2, Part 2, 4th Edition, Georg Thieme Verlag, Stuttgart 1963, *pp* 319 *et seq*.

Other cross-linking possibilities are achievable using polyisocyanates. Suitable isocyanate compounds are particularly the well known commercially available "highsolid isocyanates", hydrophilized and/or blocked isocyanates (*cf* DE-A 4,216,536).

Suitable isocyanates are the isocyanates used for the synthesis of the polyurethane and specified above as monomers (a). Of these, particularly the polyvalent isocyanates containing more than 2 isocyanate groups are preferred.

Suitable blocking agents for the isocyanates are for example alcohols and oximes, *eg* acetone oxime or methylethylketone oxime.

Cross-linking agents (B) can furthermore be polymeric resins carrying oxime-blocked isocyanate groups as described in DE-A 4,237,030, DE-A 3,345,448, WO 93/01245 and in US Patent 5,358,997.

Cross linkage of the polyurethanes (A) which are present in the aqueous dispersion of the invention, with a polyisocyanate usually takes place in the presence of a basic catalyst, *eg* a tertiary alkylamine.

With the exception of the non-blocked isocyanates and the aldimines, the dispersions of the invention are generally blended at any desired time prior to treatment with the cross-linking agent. It is equally possible to add the cross-linking agents to the polyurethane (A) prior to dispersion thereof in water, if

desired.

The dispersions of the invention may also contain other resins that are emulsifiable or dispersible in water, such as polymer resins, polyurethane resins, polyester resins, epoxide resins or alkyd resins and also commercially available auxiliaries and additives such as foaming agents, defoaming agents, emulsifiers, thickeners, levelling agents and thixotropic agents, and colorants such as dyes and pigments.

Dispersions of the invention which contain, as cross-linking agents (B), a compound containing isocyanate groups blocked with aldehyde, primary or secondary amino, hydrazine, aminoxy, hydrazide or ketoxime groups are referred to as single-component systems, since they can be processed within an arbitrary period of time following the preparation thereof.

Dispersions of the invention, to which cross-linkings agent (B) have been added which comprise a compound containing non-blocked isocyanate groups, are referred to as two-component systems, since on account of the restricted period of time in which the prepared mixture may be processed (*ca* 8 hours), mixing is usually carried out by the user of the dispersions.

The coating compositions prepared in this way are generally applied to the workpiece to be coated, by any of the methods conventionally used in the paints and coating compositions industry, that is to say, for example, by roller-coating, spraying, brush-coating, pouring or dip-coating.

Subsequent drying or final curing of the coating composition can take place both by cold curing (*ie* by drying at temperatures of from 0 to 80 °C, preferably at room temperature) or by the so-called baking methods (*ie* by drying at temperatures usually of from 80 to 280 °C).

Suitable for cold curing are primarily cross-linking agents containing aldehyde, aldimine, primary or secondary amino, hydrazine, aminoxy or hydrazide groups.

It is suspected that the polyaddition or polycondensation reaction which causes cross linkage does not take place in these systems until a large portion of the water has evaporated. The coating compositions involve therefore a single-component system comprising binding agent and cross-linking agent.

Cold curing may also be carried out in the presence of cross-linking agents (B) containing free isocyanate groups. When using this processing method the dispersion of the invention should be applied to the workpiece not later than about

8 hours following mixing with the cross-linking agent.

When use is made of (hetero)aromatic cross-linking agents (B) containing aldimine groups it is also possible to carry out cold curing. The shelf life of the dispersions of the invention ranges in such cases from one hour to several weeks depending on their composition.

When it is desired to process the coating composition following baking, suitable cross-linkings agent are particularly the aforementioned aminoplastic resins, blocked and non-blocked polyisocyanates and the Michael acceptors.

A certain degree of cross linkage of the polyurethane takes place under the conditions of the stove enamelling process even when no cross-linking agent is present. This is particularly the case when the cross linkage takes place in the presence of the Lewis or Broenstedt bases described in DE-A 4,237,492, such as tertiary amines, *eg* 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

The coating compositions of the invention are particularly suitable for painting onto wood, metal, plastics materials, for coating paper, leather, textiles, and for the preparation of shaped articles and printing inks and for use as adhesives.

The dispersions of the invention are distinguished by the fact that even when no or only relatively small amounts of levelling agents are contained therein, they can be processed to give high-grade coatings.

Furthermore, the dispersions of the invention can be processed either as single-component or two-component systems by the cold-curing method or the baking method. This is advantageous for users who work with different methods selected from these 4 processing variants, because they will only need to stock up a small number of polyurethane dispersions for the various processing methods.

On the other hand aqueous dispersions which contain the polyurethane (A) are highly suitable for the preparation of printing inks.

These printing inks preferably have the following composition:

- (I) from 15 to 30 wt-% of a binding agent, substantially consisting of the polyurethane (A) and the cross-linking agent (B)
- (II) from 7 to 15 wt% of a pigment

(III) from 2 to 5 wt% of an alcohol suitable for use as solvent

(IV) from 4.5 to 10 wt% of conventional additives

(V) from 45 to 70 wt% of water.

The cross-linking agents (B) are preferably the polyhydrazides described in detail above, which are used in the proportions specified above.

The conventional additives are auxiliaries and additives, such as are generally used in printing inks, that is to say, for example, waxes, foam depressants, dispersing and wetting agents and also microcides.

Otherwise the components (ii) to (v) used in the printing inks are those generally used in printing inks as disclosed, for example, in Ullmanns Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A22; 1993 VCH Publishers, Inc.; pp. 143 to 155.

These printing inks are particularly suitable for printing plastics films such as polyethylene or polypropylene films which have a surface tension of from 30 to 50, preferably from 35 to 40, more preferably of from 37 to 39 mN/m (measured with water at a temperature of 23 °C). Printing can be effected by conventional processes (*cf loc cit.* pp 145 and 146).

Plastics films having such surface tensions are commercially available films which have been corona-treated.

These printing inks have, in association with said recommended substrates, an advantageous wetting action. The printed films are resistant to normal mechanical stresses and solvents.

Abbreviations:

ADDH	adipic dihydrazide
IPDI	Vestanat [®] IPDI sold by Huels / isophorone diisocyanate
MHAA	N-(2-hydroxyethyl)acetoacetamide.
MEK	methyl ethyl ketone

TMP trimethylol propane

parts parts by weight

5 mw molecular weight

ok in order

Examples

10

Dispersion 1

400 Parts of a polyester of adipic acid, isophthalic acid and hexane-1,6-diol of
mw 1000 (molar ratio of the acids 1:1), 116.2 parts of MHAA (sold by LONZA),
15 40.2 parts of DMPA, 36 parts of butane-1,4-diol and 452.4 parts of IPDI were
caused to react at 90 °C in 250 parts of MEK. After 1 h, 33.6 parts of TMP were
added and the reaction was continued for 3 h at 90 °C. Following the addition of
500 parts of acetone the isocyanate concentration was 0.92 % (theory 0.76 %). 30.4
parts of triethylamine, 1900 parts of water and 8.8 parts of diethylenetriamine
20 were successively added to the pale yellow, transparent prepolymer solution to
form a milky dispersion. The solvents were removed. The solids concentration was
34.9 %. pH 7.6. Following storage of the dispersion for three months at room
temperature the properties were virtually unchanged.

25 Dispersion 1a

A mixture of 100 parts of dispersion 1, 2.77 parts of adipic dihydrazide and 20.8
parts of water; stable dispersion.

30 Comparison Dispersion 1

Comparison Dispersion 1 was prepared in a similar manner to Dispersion 1 except
that instead of MHAA, 92.9 parts of diacetone/alcohol were used. 3 hours after the
addition of TMP the NCO value was 2.65 % (theory 1.03 %); after a further two
35 hours the NCO value was still 2.43 %.

Comparison Dispersion 1a

Comparison Dispersion 1a was prepared by a variation of the process for the
40 preparation of Comparison Dispersion 1. Diacetone/alcohol and IPDI were first of

all caused to react alone at 90 °C. After 2 h there were added the polyester, hexane-1,6-diol, DMPA and MEK. After a further hour there was added TMP. 3 h after the addition of TMP the NCO concentration was 1.11 %. The batch was diluted with acetone and to the solution there were successively added triethylamine, water and diethylenetriamine to form a milky dispersion. The solvents were removed. The solids concentration was 30.8 %. pH 8.3.

After about one week's storage at room temperature the dispersion had separated into solid material and serum. In the plastics container in which the dispersion had been stored there was superatmospheric pressure.

Dispersion 2

Dispersion 2 was prepared in a similar manner to dispersion 1 using the following constituents: 400 parts of polyester, 53.7 parts of DMPA, 22.5 parts of butane-1,4-diol, 116.1 parts of MHAA, 441.3 parts of IPDI, 33.6 parts of TMP, 40.5 parts of triethylamine and 8.8 parts of diethylenetriamine. There was formed a clear, slightly yellow dispersion. The solids concentration was 33.4 %. pH 8.3.

Comparison Dispersion 2

Comparison Dispersion 2 was prepared in a similar manner to Dispersion 2 except that instead of MHAA, 70.5 parts of 4-hydroxy-2-butanone were used. During the course of prepolymer synthesis the solution turned to an intense brown to black color.

Dispersion 3

Dispersion 3 was prepared in a similar manner to dispersion 1 using the following constituents: 400 parts of a polyester of adipic acid, isophthalic acid and hexane-1,6-diol having a mw of 1000 (molar ratio of the acids 1:1), 58.1 parts of MHAA (sold by Lonza), 46.44 parts of hydroxyethyl acrylate, 40.24 parts of DMPA, 36.1 parts of butane-1,4-diol, 42.4 parts of IPDI, 33.6 parts of TMP, 30.4 parts of triethylamine and 8.8 parts of diethylenetriamine. There was formed an opaque dispersion. The solids concentration was 3.4 %. pH 7.9.

Test results

Solvent required for dispersion 1 a: 0

Pendulum Impact Test

Example	0.5h	1h	7h	1d	7d
Dispersion 1a	34	45	67	71	110

Alcohol Plasticizer and Water Vapor Tests (0 to 5; 0 = best mark)

Example	Alcohol (assessed visually) Immediately/1h/1d	Plasticizer (assessed visually) Immediately/1h/1d	Water vapor Immediately/1h/1d
Dispersion 1a	4/2-3/0-1	2-3/2-3/0-1	2-3/2-3/1

Gloss Test

Dispersion 1a: 79 %

Tests on coatings prepared using Dispersion 3

Baking Temp. (°C)	Gloss (assessed visually)	Square-cut Adhesion Test (0-5*)	Pendulum Impact Test (seconds)	Acetone Test (rs)	28% H ₂ SO ₄ Test 4h/60°C (0-5*)	38% H ₂ SO ₄ Test 24h/RT (0-5*)
30-60	ok	2-3	102	4	4	0
30-80	ok	2	115	3	4	0
30-100	ok	2-3	112	3	4	0
30-120	ok	0-1	122	5	4	0
30-140	ok	0-1	134	10	2	0
30-160	ok	0-1	153	45	0	0

* school-marking system, (0 to 5; 0=best mark)

The tests were carried out in the following manner.

Solvent required

The dispersions were placed on glass plates so as to have a dry layer thickness of about 25 μm , and solvent was added in an amount such as is necessary is to obtain a faultless film surface on drying. The necessary minimum amount to achieve this end is given in wt%.

Surface Hardness

The surface hardness (pendulum impact hardness) was determined as specified in DIN 53157 using a king tool. The number of impacts is given in the tables. In the case of Dispersion 1a, the tests were carried out at various times following application of the dispersion, as specified in the table, whilst in the case of Dispersion 3 the test was carried out immediately after baking.

Water vapor, alcohol and plasticizer tests

10

These tests were carried out according to DIN 68860B on double-layer coats of varnish on wood. The visual assessment took place immediately, 1 h and 1 d after termination of application. The results were assessed according to a school-marking system where 0 is the top mark and 5 is the bottom mark.

15

Degree of gloss

Determination of the degree of gloss was carried out according to DIN 67530 on double-layer coats of varnish on wood using a standard refractometer Laborsond sold by Byk at an angle of 60°.

20

Film formation on metal sheeting

The dispersion was applied to metal plates grade St 1405 by means of a film spreader so as to produce a coating having a wet thickness of 150 to 200 µm, which was then predried at room temperature for 10 minutes prior to baking.

25

Square-cut Adhesion Test

This test was carried out in accordance with DIN 53,151.

30

Surface Hardness

The hardness (pendulum impact hardness) of the film was determined in accordance with DIN 53,157 using a king tool. The table gives the time in seconds.

35

Acetone Test

A swab of cotton wool impregnated with the solvent was stroked forwards and backwards over a selected area of the coated metal whilst exerting slight pressure. One stroke forwards followed by one stroke backwards equals one reciprocal stroke (rs). This test was carried out over a range up to 50-100 reciprocal strokes. If no film is removed over this range, it is regarded as being cross-linked or cured.

10 28% Sulfuric Acid Test

This test was carried out according to instructions provided by the company DKH (Dr. Kurt Herberts), Wuppertal, as follows:

- 15 A small swab of cotton-wool impregnated with 28% strength sulfuric acid was placed on the test piece. Following a period of 4 hours in a circulating drier at 60°C, the sample was assessed in accordance with DIN 53,230 Tab. 1.

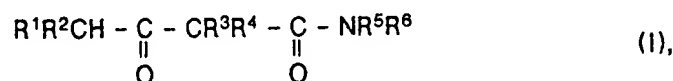
38% Sulfuric Acid Test

20

This test was carried out in a similar manner to the 28% sulfuric acid test except that the sample was left to stand for 24 hours at room temperature.

Claims

1. Aqueous dispersions, containing a polyurethane (A), mit structural units derived from compounds of formula (I)



in which the substituents have the following meanings:

$\text{R}^1, \text{R}^2, \text{R}^3$ independently denote hydrogen, $\text{C}_1\text{-C}_{24}$ alkyl or $\text{C}_6\text{-C}_{24}$ alkenyl

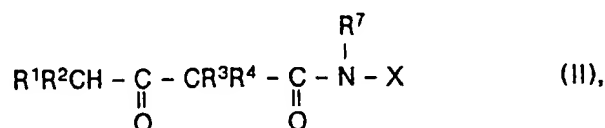
R^4 denotes hydrogen

R^5, R^6 a) together denote $\text{C}_4\text{-C}_{10}$ alkanediyl,

b) each denotes $\text{C}_2\text{-C}_{10}$ alkyl, $\text{C}_5\text{-C}_8$ cycloalkyl or $\text{C}_7\text{-C}_{20}$ aralkyl,

c) each denotes a hydroxyl-terminated poly($\text{C}_2\text{-C}_4$ alkylene oxide), or

d) one radical R^5 or R^6 has the meaning stated under (a) to (c) and the other is hydrogen or a radical of the formula II



in which

X denotes $\text{C}_2\text{-C}_8$ alkanediyl and

R^7 has the same meaning as R^5 or R^6 except that R^7 does not denote a radical of the formula II,

where

- the radicals R^5 and R^6 in each of the cases (a) and (d) carry a total of one (1) hydroxyl group attached to an aliphatic carbon atom,

- optionally the radical R⁵ and/or R⁶ carries 1 or 2 hydroxyl groups bonded to an aromatic carbon atom or one nitrile, tertiary amino, carboxylic acid or sulfonic acid group which are optionally present in the form of their salts, and
- the average functionality (F) of all structural components of the polyurethane (A) is from 1.5 to 2.2, based on the functionalities which interreact during the synthesis of the polyurethane (A) in an addition reaction.

2. Polyurethane dispersions as defined in claim 1 wherein the average functionality (F) is from 1.7 to 2.0.

3. Polyurethane dispersions as defined in claim 1 or claim 2, wherein the concentration of the carbonyl groups of the structural elements derived from the compounds of formula (I) in the polyurethane is from 3 to 140 mmol per 100 g of polyurethane (A).

4. A process for the preparation of polyurethane dispersions as defined in any of claims 1 to 3, comprising the process steps

I. Preparation of a polyurethane by causing the reaction of

a) polyvalent isocyanates containing from 4 to 30 carbon atoms,

b) polyols, of which

b1) from 10 to 100 mol, based on the total weight of the polyols (b), have a molecular weight of from 500 to 5000 and

b2) from 0 to 90 mol, based on the total amount of the polyols (b), are difunctional and have a molecular weight of from 62 to 500 g/mol,

c) compounds of the formula I,

d) optionally other polyvalent compounds containing reactive groups and differing from the monomers (b) and (c), said groups being alcoholic hydroxyl groups or primary or secondary amino groups and

e) monomers differing from the monomers (a), (b), (c) and (d) and containing at least one isocyanate group or at least one isocyanate-

reactive group and which additionally carry at least one hydrophilic group or a potentially hydrophilic group, by which means the polyurethanes are rendered water-dispersible.

5 II. Dispersion of the polyurethane obtained in step I in water.

5. Aqueous dispersions as defined in any of claims 1 to 3, containing, in addition to polyurethane (A) a cross-linking agent (B) containing at least one aldehyde group or at least 2 functional substituents selected from the
10 group consisting of primary amino group, secondary amino group, hydrazine group, hydrazide group, isocyanate group, blocked isocyanate group and aminooxy group.

6. Aqueous dispersions as defined in claim 5, wherein the amounts of component (A) and (B) are such that the molar ratio of the carbonyl
15 groups of the structural elements derived from the compounds of formula (I) to the functional substituents of the cross-linking agent (B) is from 0.5:1 to 5:1.

7. Aqueous containing dispersions as defined in any of claims 1 to 6, containing:

- 20 (I) from 15 to 30 wt% of a binding agent, essentially consisting of polyurethane (A) and the cross-linking agent (B)
- (II) from 7 to 15 wt% of a pigment
- 25 (III) from 2 to 5 wt% of an alcohol that is suitable for use as solvent
- (IV) from 4.5 to 10 wt% of conventional additives
- 30 (V) from 45 to 70 wt% of water.

8. Aqueous dispersions as defined in claim 7, containing polyhydrazides as cross-linking agents (B).

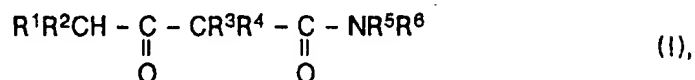
35 9. A process for coating wood, glass, plastics material, leather, paper or metal, wherein an aqueous dispersion as defined in any of claims 5 to 8 is applied to any of said substrates and dried.

10. A process for printing paper or metal foils or plastics films,
40 wherein said media are printed with a dispersion as defined in claim 7 or claim 8.

11. A process as defined in claim 10, wherein the medium printed is a plastics film having a surface tension of from 30 to 50 mN/m.
12. Objects whenever produced by the process defined in any of claims 9 to 11.

ABSTRACT OF THE SPECIFICATION:

Aqueous dispersions containing a polyurethane(A) having structural units derived from compounds of the formula (I)

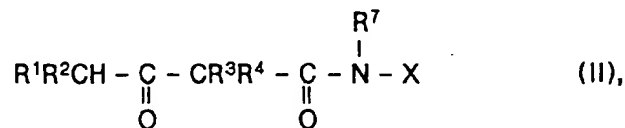


in which the substituents have the following meanings:

$\text{R}^1, \text{R}^2, \text{R}^3$ independently denote hydrogen, $\text{C}_1\text{-C}_{24}$ alkyl or $\text{C}_6\text{-C}_{24}$ alkenyl

R^4 denotes hydrogen

- R^5, R^6
- a) together denote $\text{C}_4\text{-C}_{10}$ alkanediyl,
 - b) each denotes $\text{C}_2\text{-C}_{10}$ alkyl, $\text{C}_5\text{-C}_8$ cycloalkyl or $\text{C}_7\text{-C}_{20}$ aralkyl,
 - c) each denotes a hydroxyl-terminated poly($\text{C}_2\text{-C}_4$ alkylene oxide), or
 - d) one radical R^5 or R^6 has the meaning stated under (a) to (c) and the other is hydrogen or a radical of the formula II



in which

X denotes $\text{C}_2\text{-C}_8$ alkanediyl and

R^7 has the same meaning as R^5 or R^6 except that R^7 does not denote a radical of the formula II,

where

- the radicals R^5 and R^6 in each of the cases (a) and (d) carry a total of one (1) hydroxyl group attached to an aliphatic carbon atom,
- optionally the radical R^5 and/or R^6 carries 1 or 2 hydroxyl groups bonded to an aromatic carbon atom or one nitrile, tertiary amino, carboxylic acid or sulfonic acid group which are optionally present in the form of their salts, and
- the average functionality (F) of all structural components of the polyurethane (A) is from 1.5 to 2.2, based on the functionalities which interreact during the synthesis of the polyurethane (A) in an addition reaction.